

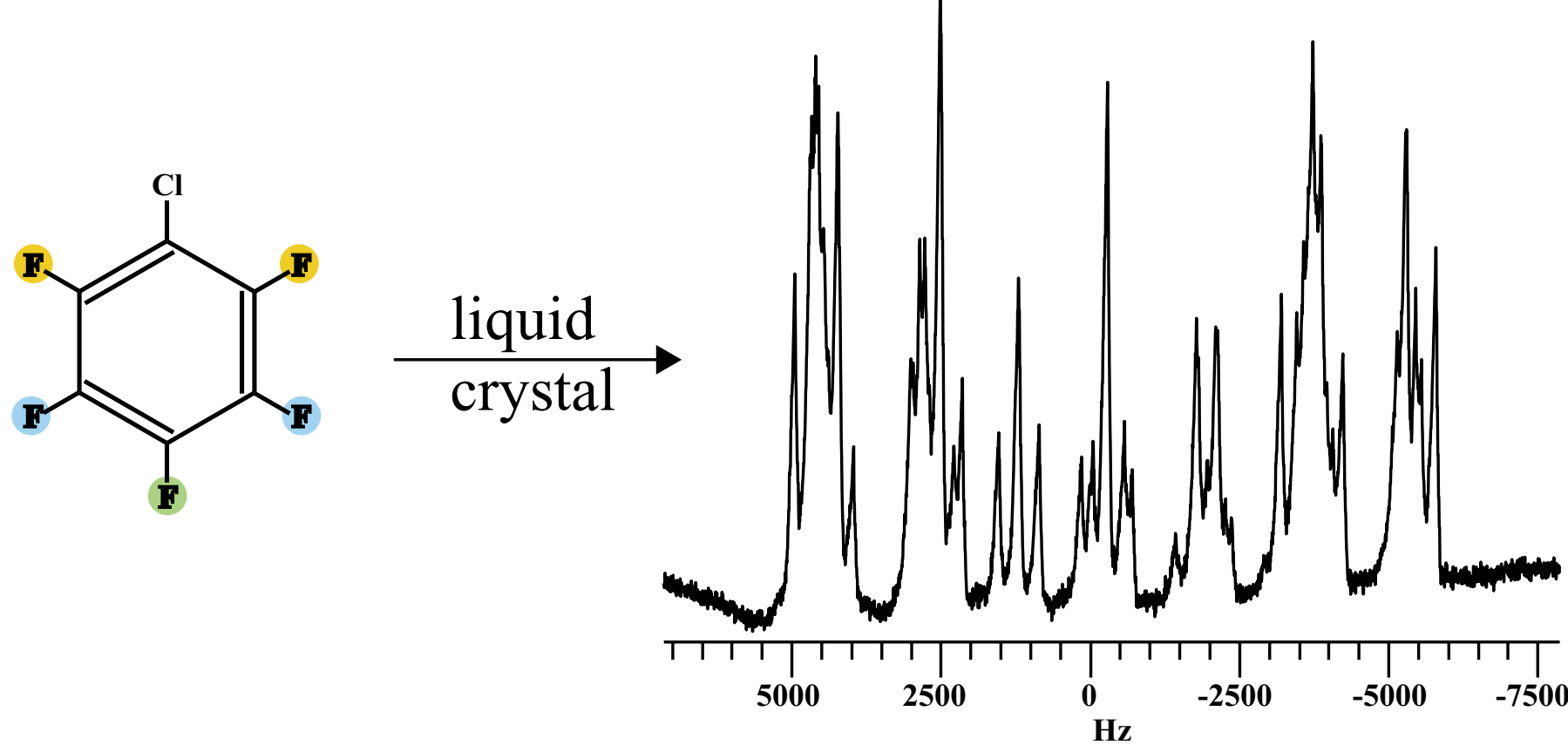
Dipolar Couplings in Liquid Crystals and Solids: Measurement and Assignment Using Novel Techniques

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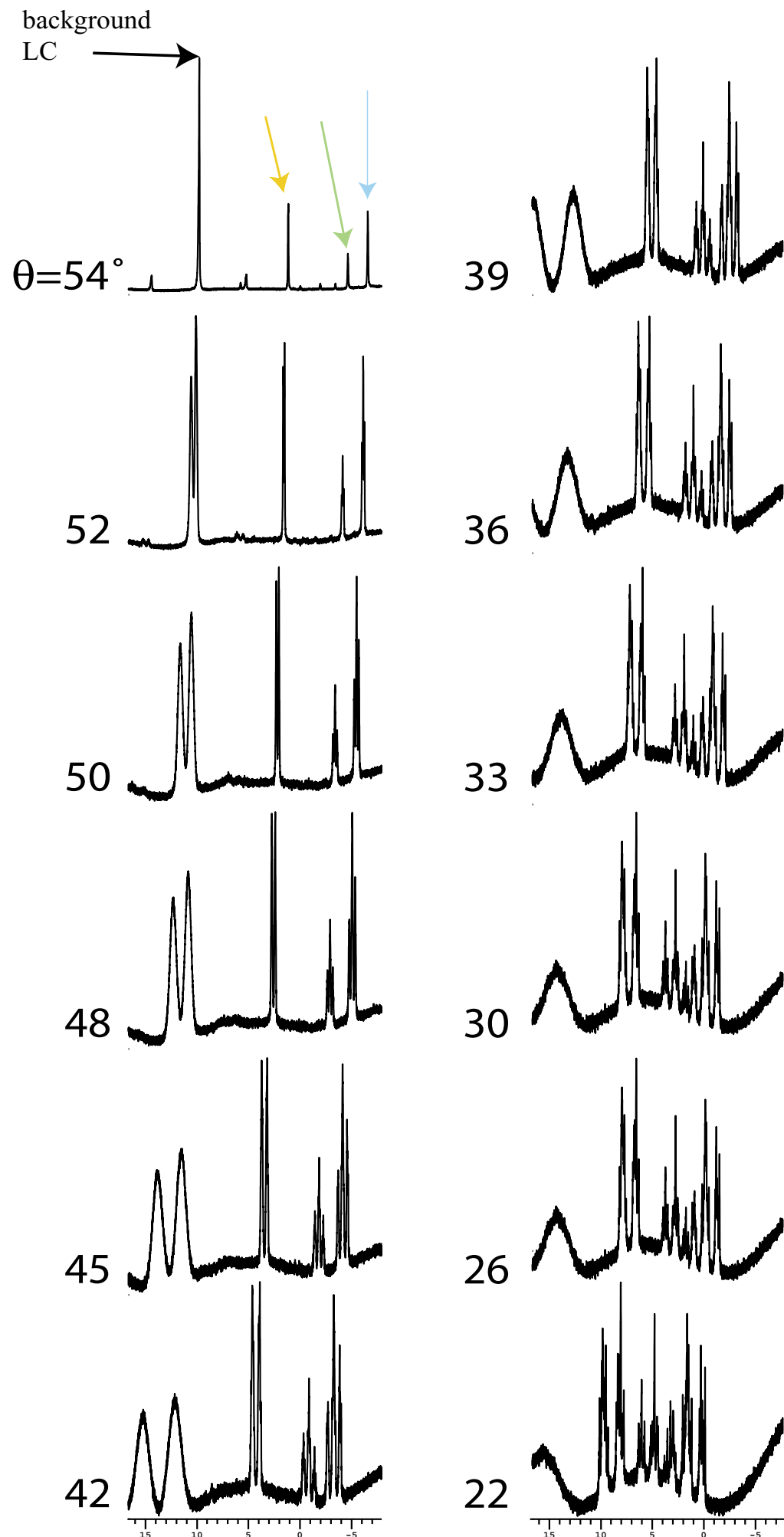
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Summary: Utilizing the 1/r³ dependence of dipolar coupling for structure determination remains a challenging goal of NMR spectroscopy . We present here two methods which are applicable for the determination of dipolar couplings in liquid crystals and solids.

Second Order Dipolar Couplings in Oriented Liquid Crystals

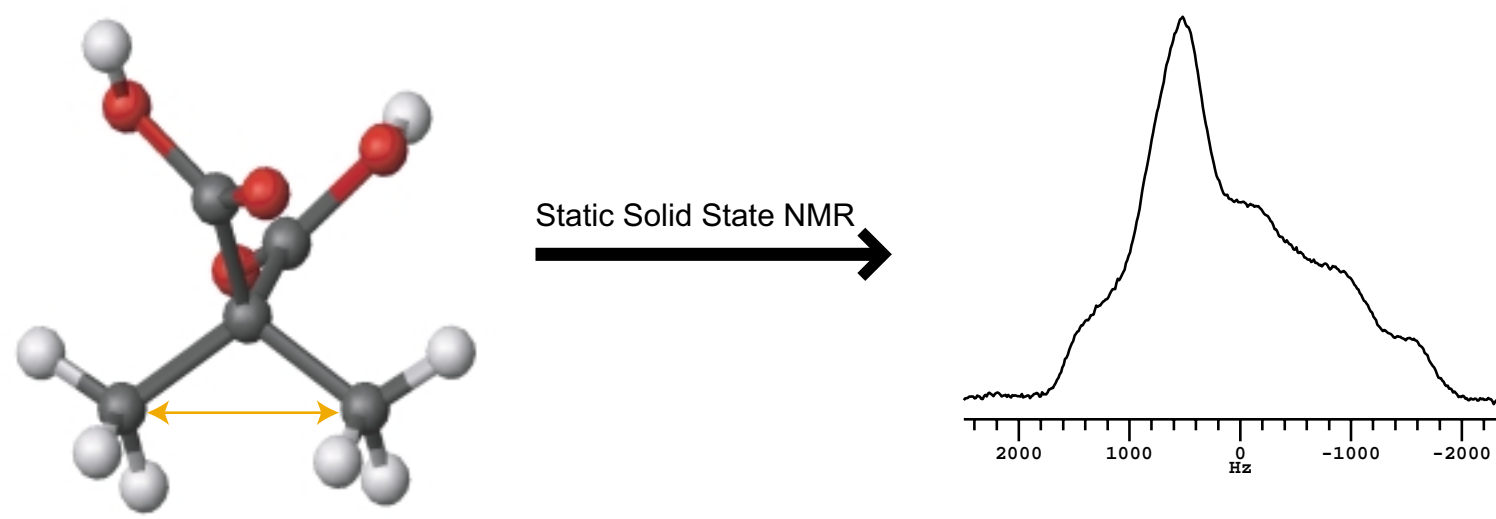
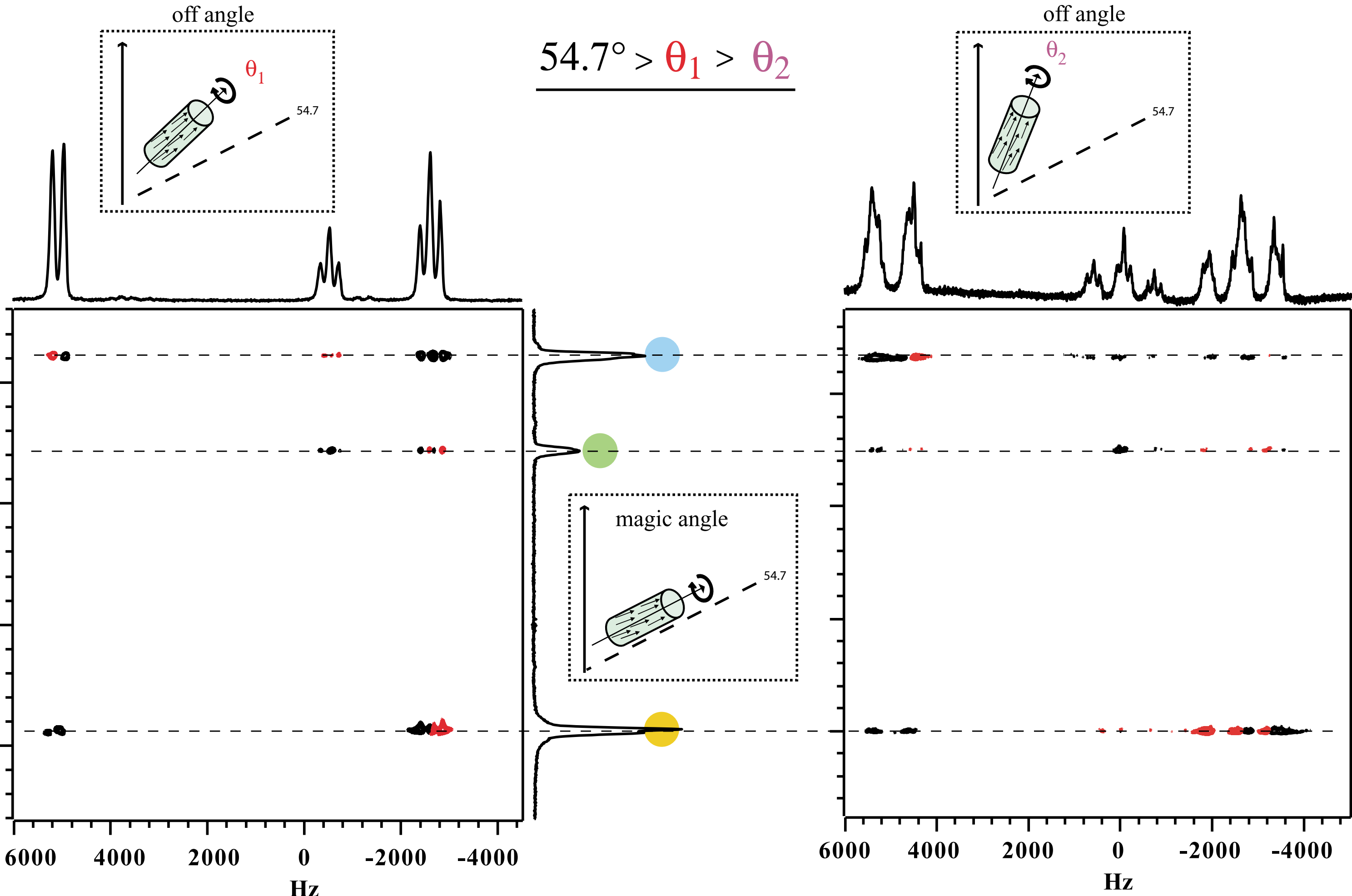


The simple molecule perfluorochlorobenzene produces a second order¹⁹F spectrum when dissolved in the liquid crystal (LC) 152. However, this spectrum can be simplified to yield readily assignable dipolar couplings by rotating the sample at an angle θ with respect to the magnetic field(1). By spinning the sample, the director of the liquid crystal reorients to align parallel to the spinning axis; thus the uniaxial motion of the liquid crystals averages the interactions. The dipolar couplings that create the second order spectrum are then scaled by $(3\cos^2\theta - 1)/2$. As shown to the right.



Switched angle spinning 2D correlation

As shown above, rotating the sample at the magic angle can reduce a complicated second order spectrum to a simple first order spectrum, and even completely average the dipolar couplings to yield an isotropic spectrum. Using this principle, the evolution of the oriented liquid crystal sample above was correlated in a 2D experiment (shown to the right) creating the first order dipole coupled spectrum in one dimension and the isotropic spectrum in the second dimension. The crosspeaks readily provide assignment of the isotropic shifts of the coupling pairs. In addition, a second 2D correlation was performed such that the couplings were approaching second order in the first dimension. The crosspeaks now reveal couplings off all spins to each other; thus the onset of a second order type spectrum.

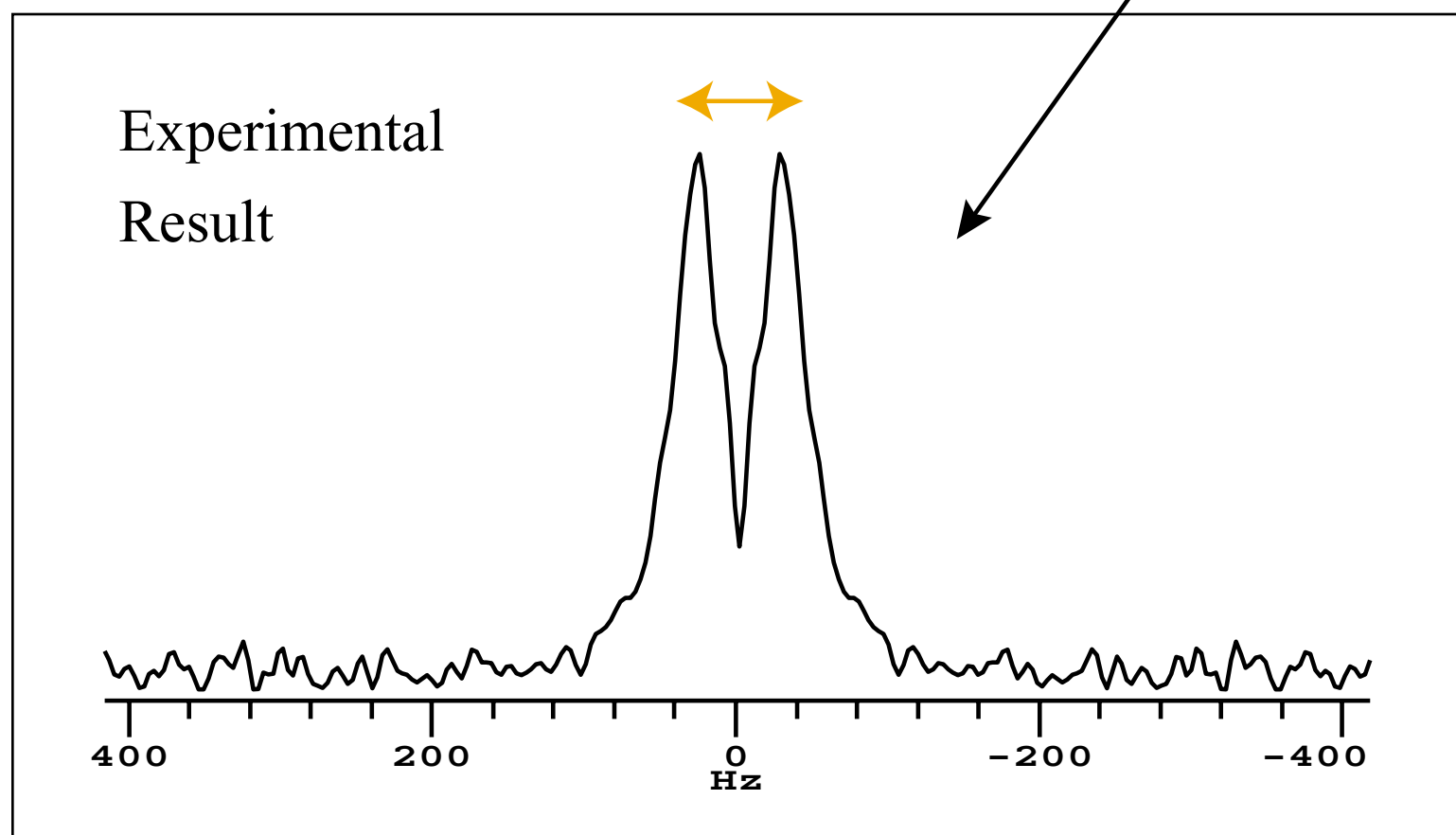
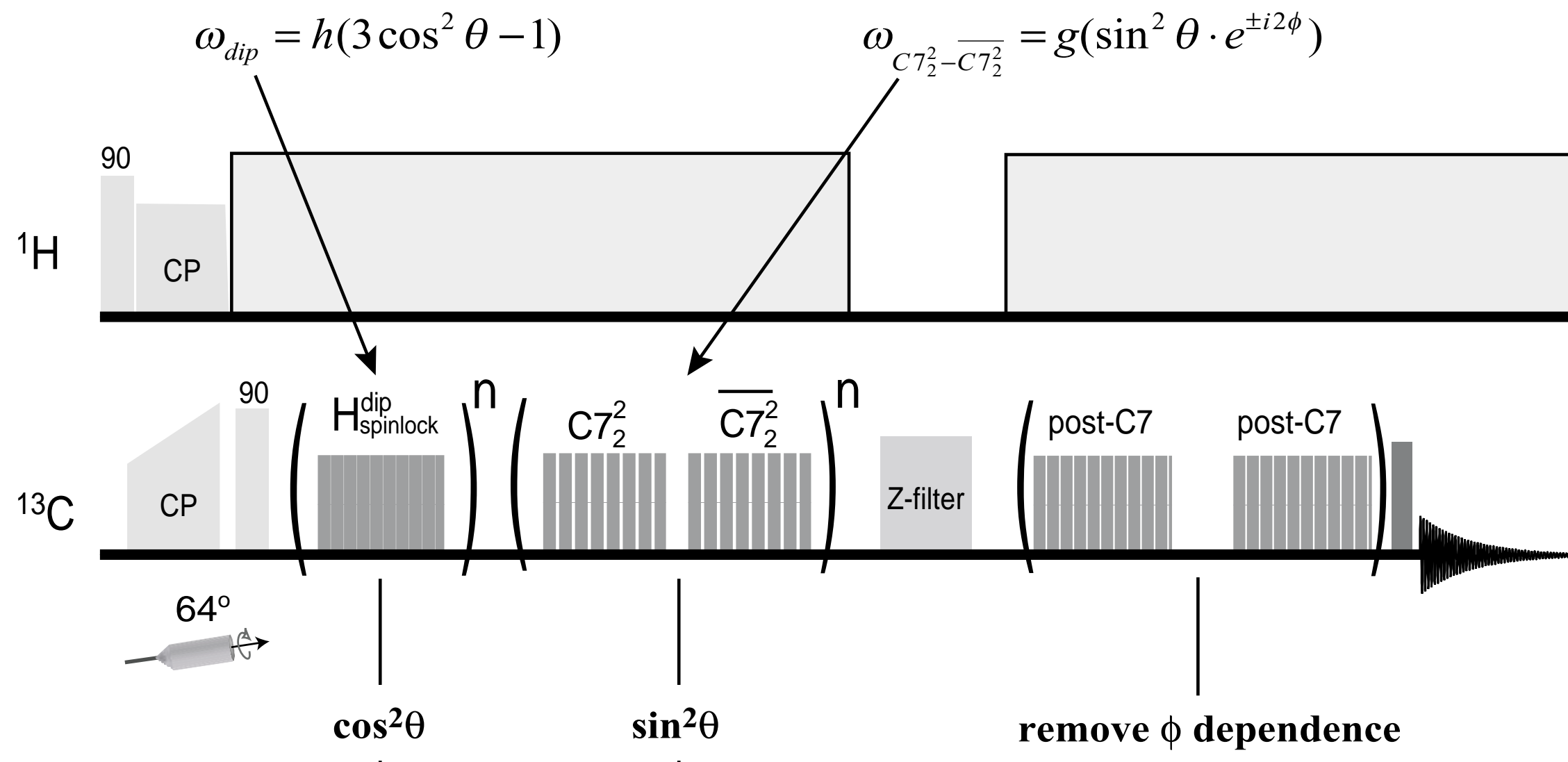


Characteristic solid state NMR spectra include broad lines such as the one shown above for dimethyl malonic acid. The broad nature of the lines are the result of the spatial (θ, ϕ) dependence of the dipolar coupling and chemical shift anisotropy. Ideally, an experiment would observe the interatomic distance dependent dipolar coupling without the θ, ϕ dependence, leaving just a scalar value. Previous experiments did this by shuttling or creating the zero-field hamiltonian using RF pulses(2,3). Here we demonstrate an alternate method to create an isotropic dipolar spectrum using a series of recoupling sequences based on C7(4).

$$\begin{aligned} \rho(0) = I_z^1 + I_z^2 &\xrightarrow{H = \omega_D h(\theta)(3I_z^1 I_z^2 - I^1 I^2)} \rho(t) = \cos\left(\frac{3}{2}\omega_D h(\theta)t\right)I_z + i\sin\left(\frac{3}{2}\omega_D h(\theta)t\right)(T_{3,2} - T_{2,-2}) \\ &= \rho_o(t) + \rho_2(t) \\ H^{EVO} = \omega_D(gA_{2,-2}T_{2,2} + gA_{2,2}T_{2,-2}) &\rightarrow \langle I_z(t, \tau) \rangle_1 = \text{Tr}(\rho_o(t, \tau)I_z) = \cos(\omega_D h(\theta)t) \cos(\omega_D g(\theta)\tau) \\ \langle I_z(t, \tau) \rangle_2 = \text{Tr}(\rho_2(t, \tau)I_z) &= -\cos(2\phi) \sin(\omega_D h(\theta)t) \sin(\omega_D g(\theta)\tau) \\ H_{2,1}^{DET} = \omega_D f(A_{2,1}T_{2,2} - A_{2,1}T_{2,-2}) &\rightarrow \langle I_z(t, \tau) \rangle_1 = -\cos(\omega_D h(\theta)t) \cos(\omega_D g(\theta)\tau) \sin^2(\omega_D f(\theta)\tau_{DET}) \\ \langle I_z(t, \tau) \rangle_2 = \cos^2(2\phi) \sin(\omega_D h(\theta)t) \sin(\omega_D g(\theta)\tau) \sin^2(\omega_D f(\theta)\tau_{DET}) & \\ S_1 \pm 2S_2 \propto \cos(\omega_D[h(\theta)t \pm g(\theta)\tau]) & \\ \propto \cos\left[\frac{3}{4}\omega_D t(3\cos^2(\theta) - 1) \pm \frac{3}{2}\omega_D \tau \sin^2(\theta)\right] &\text{final signal} \\ \sigma = \frac{3ht}{2(t+\tau)} \omega_D \sim 0.14\omega_D &\text{scaling factor} \end{aligned}$$

Creating Isotropic Dipolar Couplings in Solids

Use $\sin^2\theta + \cos^2\theta = 1$ to remove the θ dependence of the dipolar coupling



Pulse Sequence Details

experiment	phase (deg)	global added phase	recive phase
X1	0	0	-1
X2	0	90	1
Y1	90	0	-1
Y2	90	90	1
2x X3	0	0	reverse order 1
2x X4	0	90	reverse order -1
2x Y3	90	0	reverse order -1
2x Y4	90	90	reverse order 1

Times: $t_1 = t_2 = 2\omega_D$ $t_3 = t_4 = 4\omega_D$ $t_5 = 6\omega_D$ $t_6 = 8\omega_D$

Future Work:

The correlations demonstrated in liquid crystals are a simple test case and we hope to apply these methods on more complex samples where useful structural information may be obtained.

The isotropic dipolar coupling experiment in solids is demonstrative of the principle of combining evolutions to create isotropic spectra. The goal of this work is to eventually apply this method to heteronuclear couplings where the associated scaling factor becomes less important.

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